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Reactivity and Ligand Dynamics of a Skeletally Chiral Metal Cluster: $[(\mu_3\text{-}\eta^2\text{-}C_2{}^tBu)(CO)_9Ru_3]_2(\mu_4\text{-}Hg)$

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Received June 14, 1988

The reaction chemistry and ligand dynamics of $[Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_2{}^tBu)]_2(\mu_4\text{-}Hg)$ (**3**) have been studied. It has been found that phosphine substitution can be affected thermally, photochemically and by electron transfer. In all cases the same substitution products are observed: $[Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_2{}^tBu)](\mu_4\text{-}Hg)\text{-}[(Ru_3(CO)_8(\mu_3\text{-}\eta^2\text{-}C_2{}^tBu)(PPh_3)]$ (**4a**), $[Ru_3(CO)_8(\mu_3\text{-}\eta^2\text{-}C_2{}^tBu)(PPh_3)]_2(\mu_4\text{-}Hg)$ (**4b**), and $[Ru_3(CO)_8(\mu_3\text{-}\eta^2\text{-}C_2{}^tBu)(PPh_3)](\mu_4\text{-}Hg)[Ru_3(CO)_7(\mu_3\text{-}\eta^2\text{-}C_2{}^tBu)(PPh_3)_2]$ (**4c**). Compound **3** shows high thermal stability with respect to reductive elimination of Hg metal. However, redistribution reactions occur at elevated temperatures. The redistribution equilibrium constant is found to be 0.10 at 80 °C for the monophosphine derivative $[Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_2{}^tBu)](\mu_4\text{-}Hg)[Ru_3(CO)_8(\mu_3\text{-}\eta^2\text{-}C_2{}^tBu)(P(Ph)_2(CH_2CH_2COOC_2H_5))]$ (**4d**). The thermal reaction of **3** with H_2 gives $H_3Ru_3(CO)_9(\mu_3\text{-}\eta^1\text{-}CCH_2C(CH_3)_3)$ (**5**), $HRu_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_2{}^tBu)$ (**1**), $H_4Ru_4(CO)_{12}$, and Hg metal as the major products. The photochemical reaction of **3** and H_2 yields the same products except $H_4Ru_4(CO)_{12}$ is not produced under these conditions. When **3** is reacted with zinc metal, transmetalation is observed to give $[Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_2{}^tBu)_2](\mu_4\text{-}Zn)$ and Hg metal. Reaction of **3** with Br_2 gives the cleavage product $(CO)_9(\mu_3\text{-}\eta^2\text{-}C_2{}^tBu)Ru_3HgBr$ (**2b**) while reaction with HCl gives **1** and $(\mu_3\text{-}\eta^2\text{-}C_2{}^tBu)(CO)_9Ru_3HgCl$ (**2c**). Variable-temperature ^{13}C and ^{31}P NMR of **3**, **4a**, and **4b** reveal axial–radial exchange processes similar to those observed for related compounds. Variable-temperature ^{31}P NMR of a mixture of the diastereomers of $[Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_2{}^tBu)](\mu_4\text{-}Hg)[Ru_3(CO)_8(\mu^3\text{-}\eta^2\text{-}C_2{}^tBu)(P\text{-}(CH_3)(C_6H_5CH_2)(C_6H_5))]$ (**4f** and **4f′**) shows racemization at high temperatures which is interpreted as a rearrangement of the metal skeleton from its chiral ground state to a symmetrical structure containing a face-bridging mercury.

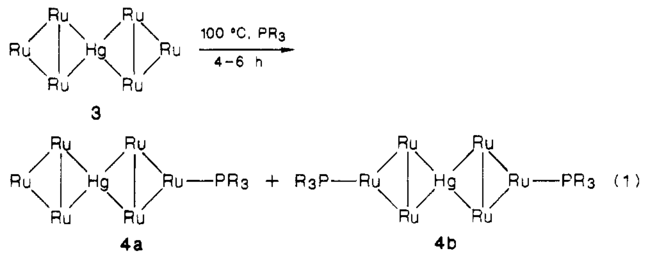
Introduction

Transition-metal compounds containing two-coordinate mercury atoms are well represented in the chemical literature.[1] In 1980, we reported the introduction of the HgX^+ moiety, replacing the H^+, in the trimetallic skeleton of $HRu_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_2{}^tBu)$ (**1**) to form a novel class of compounds: $[Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_2{}^tBu)](\mu\text{-}HgX)$ (where X = I (**2a**), Br (**2b**),[2] $[Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_2{}^tBu)]$ (**3**)). These compounds are characterized by delocalized, three-center, two-electron bonds involving the mercury and two of the three ruthenium atoms of the Ru_3 triangle. In particular, the crystal structure of **3** reveals a four-coordinate mercury atom bridging the edges of the two triruthenium framgnets (Figure 1).[3] Since our initial report, other compounds containing delocalized mercury transition-metal bonds with mercury coordination numbers of four,[4-7] five,[8] and six[9] have been reported. These compounds that feature electron-deficient, delocalized bonding to mercury have become increasingly familiar, but their chemistry has not been studied. We report here studies on the reactivity of **3** for comparison with the well-characterized two-center, two-electron mercury transition-metal bond.

In addition, compound **3** belongs to a special class of chiral molecules in that if one allows for localized exchange of carbonyl groups on the wing tip Ru atoms the molecule possesses a C_2 axis yet is still chiral by virtue of the screw axis associated with the metal skeleton. Similar chiral "skeletons" have been noted in spiro-organic compounds. We report here a variable-temperature ^{13}C NMR and ^{31}P NMR study which reveals the ligand scrambling processes in **3** and its phosphine derivatives and information concerning the rigidity of its chiral metal skeleton.

Results and Discussion

A. Thermolysis of 3 with Trialkyl- (or Triaryl-) Phosphines When **3** is thermolyzed at 100–110 °C in the presence of trialkyl- or triarylphosphines, substitution of a CO ligand takes place on one or both of the wing-tip ruthenium atoms to form the mono- and bis(phosphine) derivatives of **3** (eq 1). In the case of triphenylphosphine, prolonged reaction with excess phosphine also gives a trisubstituted derivative where the third phosphine is substituted on one of the mercury-bridged edges of the cluster (eq 1) as evidenced from observation of two signals, one showing two-bond mercury–phosphorus coupling in the ^{31}P NMR. The phosphine-substituted derivatives **4a–f** for a range of trialkylphosphines were characterized by ^{31}P, ^{13}C, and ^1H NMR, IR, and elemental analyses. Structural assignments are based on comparison of ^{31}P and ^{13}C NMR data for the closely related **2** and $(P(C_6H_5)_3)(CO)_8(\mu_3\text{-}\eta^2\text{-}C_2{}^tBu)Ru(\mu_3\text{-}Hg)Mo(\eta\text{-}C_5H_5)(CO)_3$.[2,3] (The acetylido ligand and the carbonyl groups are omitted in all equations involving **3** and its derivatives for clarity.)



Typical yields of the phosphine derivatives of **3** are 25–35% for the mono(phopsphine) species and 20–30% for the bis(phosphine) species when 1 equiv of phosphine is reacted. These yields can be varied, however, by changing the amount of phosphine used or by changing

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(1) Meyer, T. *Prog. Inorg. Chem.* **1975**, *19*, 14.

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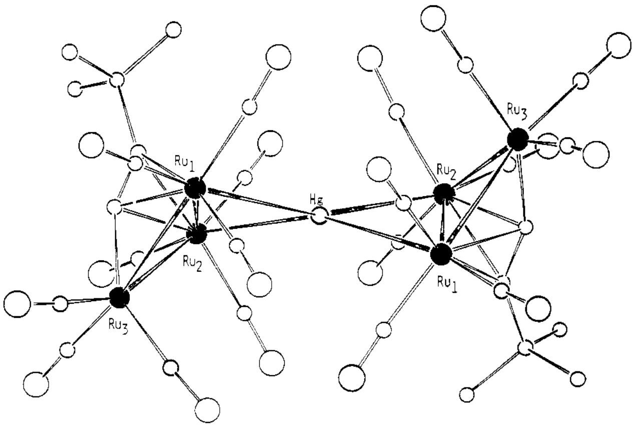
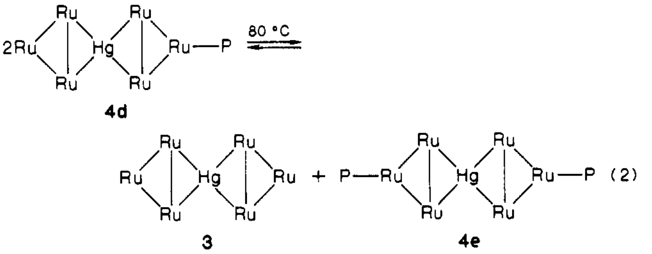


Figure 1. Solid-state structure of 1 (from ref 3).

the reaction time. As expected, an increase in either of these variables increases the amount of bis(phosphine) product and produces some of the trisubstituted derivative. Phosphine substitution can also be affected photochemically at ambient temperatures.

B. Thermolysis of 3. Compound 3 exhibits considerable thermal stability, surviving 5 days of reflux in toluene (110 °C) in CO atmosphere. As long as the thermolysis is performed under a CO atmosphere, no decomposition is observed. However, if the CO atmosphere is replaced by N_2, nonspecific decomposition of the cluster ensues as a result of CO dissociation from the cluster but not from direct reductive elimination of the mercury.

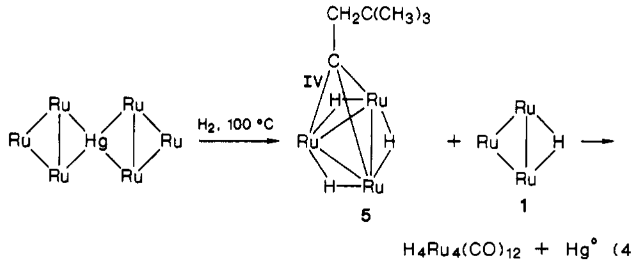
Although no Hg elimination is observed, the mercury bonds in 3 are cleaved at elevated temperature resulting in a redistribution reaction characteristic of mercury compounds.[10] This process is evident when the monophosphine derivative **4d** is heated under a CO atmosphere at 80 °C for 11 h. (eq 2).



The equilibrium constant for the above reaction at 80 °C was measured by ^1H NMR of the reaction mixture and by chromatographic separation of the reaction products and found to equal 0.10 (eq 3). This equilibrium mixture can be approached from both sides since equimolar mixtures of 3 and **4e** give **4d** in about the same relative amounts.

$$K_{80\,°C} = [\mathbf{3}][\mathbf{4e}]/[\mathbf{4d}]^2 = 0.10 \qquad (3)$$

C. Thermolysis of 3 with H_2. The reaction of 3 with hydrogen gas in refluxing hydrocarbon solvents yields several products (eq 4). The first product is 1, formed from the addition of 1 mol of H_2 to the cluster and cleavage of the metal framework by reductive elimination of Hg metal. In addition to 1, a reduction product, $H_3Ru_3(CO)_9(\mu_3\text{-}CCH_2C(CH_3)_3)$ (5), is formed from the addition of two additional moles of H_2 to each triruthenium fragment. The acetylene moiety in 5 has been transformed from a μ_3-η^2-bound ligand to a μ_3-η^1-methylidyne-capping ligand. The compound $H_4Ru_4(CO)_{12}$ is apparently produced from the thermal decomposition of the triruthenium clusters followed by condensation of the unsaturated ruthenium fragments. The same product distribution is also observed when 1 is reacted directly with hydrogen gas.[11] Both clusters 1 and 3 show a marked rate dependence for reduction on the presence of carbon monoxide. If the above reactions are attempted under a mixed atmosphere of hydrogen and carbon monoxide, the reaction is effectively shut down. This observation clearly points to the need for CO dissociation to take place during or prior to the rate-determining step. The CO dissociation presumably opens a coordination site on one of the metals, allowing oxidative addition of H_2 which then migrates from the metal framework to the organic moiety. The lost CO ligand must then be recoordinated to form the final products 1 and 5.



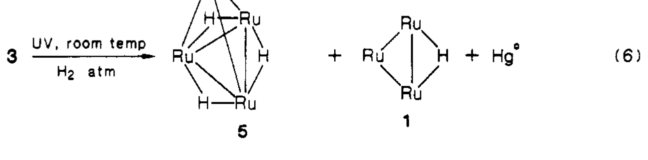
$H_4Ru_4(CO)_{12}$ + $Hg^°$ (4)

D. Photolysis of 3. Mercury atoms bound to both organic and transition-metal ligands have a rich photochemistry.[12] The most common photochemical reaction of mercury compounds in the reductive elimination reaction[13] (eq 5). This is typically a facile reaction for transition-metal compounds containing mercury in two-center, two-electron bonds. However, when compound 3 is irradiated with UV light in either a Pyrex or a quartz reaction vessel under a CO atmosphere, no reaction takes place.

$$(C_6F_5)_3Ge\text{-}Hg\text{-}Pt(PPh_3)_2\text{-}Ge(C_6F_5) \xrightarrow[30\ \text{min}]{h\nu} [(C_6F_5)_3Ge]_2Pt(PPh_3)_2 + Hg^0 \quad (5)$$

The delocalized three-center, two-electron bonds of mercury in compound 3 are extremely photochemically stable. However, the photolysis must be run under a carbon monoxide atmosphere, otherwise CO dissociation ensues leading to some nonspecific decomposition of the cluster. Facile phosphine substitution can be accomplished by photolyzing 3 in the presence of a trialkyl- (or triaryl-) phosphine. Both the mono- and bis(phosphine) derivatives of 3 can be obtained in this fashion.

E. Photolysis of 3 with H_2. When compound 3 is photolyzed in the presence of H_2, the same reduction products are formed as when the reaction is performed under thermal conditions (eq 6).



The only difference is that the decomposition product $H_4Ru_4(CO)_{12}$ is not formed under photochemical conditions, suggesting that photofragmentation of the Ru_3

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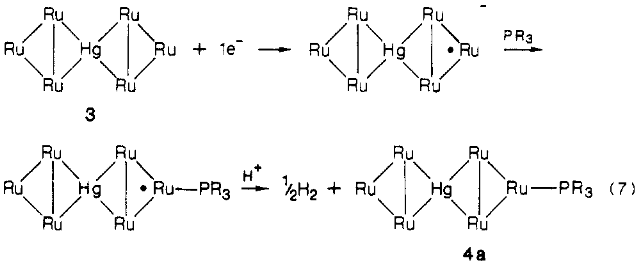
moieties is not a facile process.

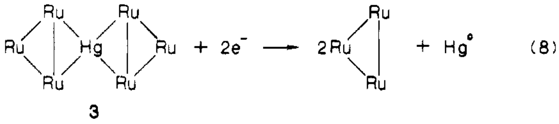
F. Reduction of 3 with Sodium Benzophenone Ketyl. When compound 3 is reacted with 1 equiv of sodium benzophenone ketyl, it appears from the observed color change from blue to red that an electron transfer takes place to form the radical anion of 3. Previous studies have suggested that the odd electron is thought to populate a π^*-antibonding molecular orbital which has the effect of reducing the bond order of the metal framework.[14] Opening of the weakened Ru–Ru bond results in a coordinatively unsaturated ruthenium center which then is subject to attack by a variety of nucleophiles.[14]

When the one-electron reduction of 3 is performed in the presence of $P(C_6H_5)_3$ (or $(C_6H_5)_2P(CH_2CH_2COOC_2H_5)$), conversion to the mono(phosphine)-substituted derivative **4a** (or **4d**) is observed (eq 7).



Once the radical anion coordinates the trialkylphosphine, reoxidation of the cluster is accomplished in a dilute acidic workup. Electron transfer does not take place from the phosphine-substituted radical anion to another mole of 3, as this would constitute a catalytic process which is not observed.

When 3 is reacted with 2 equiv of sodium benzophenone ketyl, the central mercury acts as a two-electron sink, fragmenting the cluster into Hg metal and two stable triruthenium anions (eq 8) which are isolated quantitatively as 1 after acid workup. If the two-electron reduction

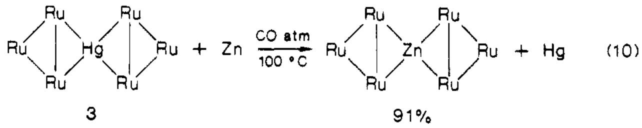


is done in the presence of a phosphine, phosphine-substituted derivatives of 1 are obtained. This indicates that the initial electron transfer is to the triruthenium cluster which opens the coordination site on the ruthenium atom. The electron must eventually migrate to the mercury center to form the observed products.

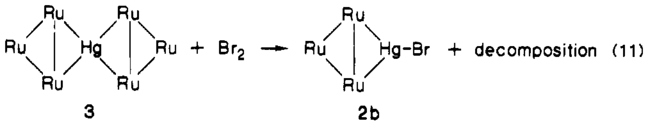
G. Reaction of 3 with Zn. Another typical reaction of mercury–transition-metal complexes is transmetalation: the substitution of other metals for mercury without disrupting the metal framework in any other way. Mercury is known to transmetalate under very mild conditions[15] with the other members of its triad when it is bound to two transition-metal centers (eq 9).

$$Hg[Co(CO)_4]_2 \xrightarrow[\text{10 min}]{\text{Zn, 25 °C}} Zn[Co(CO)_4]_2 + Hg \qquad (9)$$

When 3 was reacted with Zn metal at 110 °C for 14 h under a CO atmosphere, the expected transmetalation reaction is observed (eq 10). The Zn-containing product formed only after refluxing in toluene for an extended period and its identity was confirmed by elemental analysis. These are much more vigorous conditions than those required for transmetalation of two-center, two-electron mercury–transition-metal bonds.[15]



H. Reaction of 3 with Br_2. The reaction of 3 with Br_2 was first reported by King.[16] The cluster is cleaved at the mercury center by the Br_2 to yield the known cluster **2b** and unidentified decomposition products (eq 11).



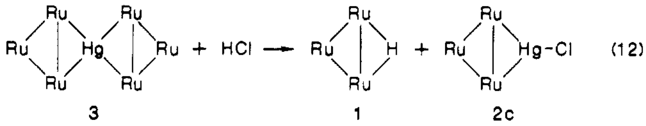
In an attempt to identify the unknown products, the reaction was reexamined and a dependence on light was observed. When the reaction is carefully protected from ambient light, no reaction is observed. It is only after the reaction mixture is exposed to light that the product **2b** is formed. This clear dependence on light suggests that bromine radicals are required for initiation of this reaction. None of the other reactions presented here show a dependence on light.

The coproduct of the reaction is thought to be the 50-electron cluster containing the bridging three-electron-donating bromine ligand, $(\mu\text{-Br})Ru_3(CO)_9(C_2{}^tBu)$.[16] However, all attempts to isolate this unstable complex have been unsuccessful.

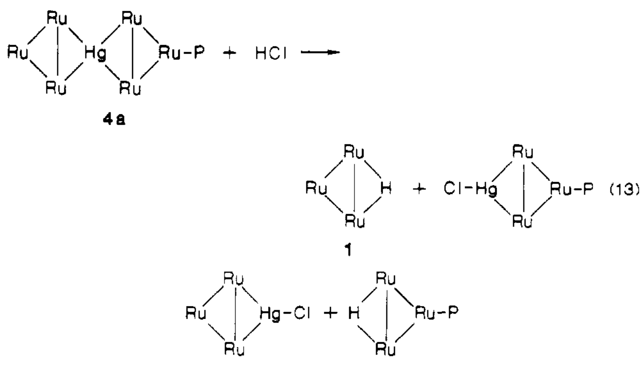
I. Reaction of 3 with HCl. Mercury compounds are known to undergo cleavage reactions of the type:[17] When

$$R\text{–}Hg\text{–}R + HCl \rightarrow RH + Cl\text{–}Hg\text{–}R$$

compound 3 is reacted with HCl in a toluene solution, an analogous reaction is observed (eq 12). Phosphine sub-



stitution on a trinuclear cluster makes the cluster more electron-rich and therefore more basic toward protonation. The cleavage process (eq 12) does not show a dependence on the basicity of the triruthernium fragments bound to the mercury atom. When the mono(phosphine) derivative **4a** is reacted with HCl, a combination of the four possible cleavage products are obtained (eq 13) as evidenced by comparative TLC and ^1H NMR analysis of the reaction mixture. This result suggests that protonation of the triruthenium fragment is not directly involved in the



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[15] Burlitch, J. M. *J. Organomet. Chem.* **1967**, *90*, 9.
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[17] Kochi, J., Ed. *Free Radicals*; Wiley-Interscience: New York; 1900; Vol. 1, p 575.

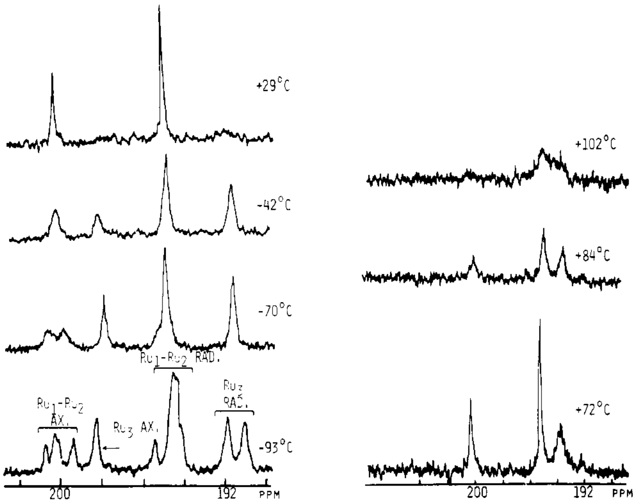
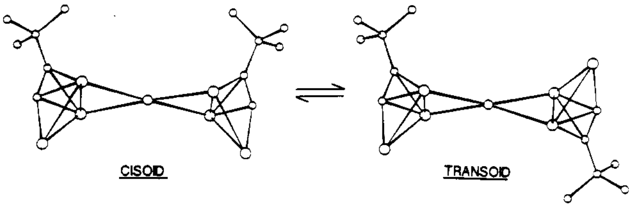


Figure 2. Variable-temperature ^{13}C NMR of **3** in the carbonyl region from -93 to +102 °C (CD_2Cl_2, -93 to -40 °C; $C_6D_5CD_3$, -40 to +102 °C). Numbering refers to Figure 1 (AX = axial; RAD = radial carbonyls).

Scheme I



cleavage mechanism. This is consistent with what has been found for other electrophilic cleavage reactions of mercury compounds where a four-centered transition state is suggested in nonpolar solvents such as toluene.[17]

J. Reaction of 3 with Ethanethiol. When compound **3** is reacted with ethanethiol at 50 °C, a cleavage reaction is observed that produces the known cluster **1** and an intractable precipitate.

The orange, sulfur-containing precipitate could not be further identified because of its insolubility in all organic solvents. This compound is probably an oligomeric thiol-bridged mercury complex.

K. Variable-Temperature ^{13}C NMR. The variable-temperature ^{13}C NMR spectra in the carbonyl region of compounds **3**, **4a**, and **4b** were measured from -93 to +102 °C in CD_2Cl_2 and toluene-d_8. The averaging of the carbonyl ligands in these compounds follows the general pattern observed for $(\mu_3\text{-}\eta^2\text{-}C_2{}^tBu)(CO)_9Ru_3(\mu\text{-}X)$ (X = H, HgBr) above -42 °C.[2] The first stage of exchange involves axial–radial exchange at the unique ruthenium atoms. However, there is a significant increase in the barrier to the second stage of exchange, axial–radial exchange of the carbonyls on the mercury-bridged ruthenium atoms, and in the temperature at which complete carbonyl scrambling becomes rapid on the NMR time scale as compared with **1** and **2**.

A complete and unequivocal explanation of the observed changes in the variable-temperature ^{13}C NMR of **3** between -93 and -42 °C is not possible at this time. Since the molecule possesses a C_2 axis of symmetry, one expects to see nine resonances of equal intensity for the carbonyl groups at the low-temperature limit. Instead at -93 °C 14 broad partially resolved resonances are observed at 191.1 (2), 191.8 (2), 194.5 (3), 195.4 (1), 198.2 (2), 199.3 (1), 200.1 (1), 200.3 (1), and 200.7 (1) ppm (Figure 2, relative intensity given in parentheses). Below this temperature precipitation of **3** prevented observation of the spectrum in $CD_2Cl_2/CFCl_3$ mixtures. One likely explanation for these anomalous results is that **3** could exist, in solution, as two isomers, which differ by the relative orientation of the organic ligand (cisoid vs transoid, Scheme I). Above -42 °C these isomers could be rapidly interchanging on the NMR time scale by a ~90° oscillation of the two triruthenium rings around the mercury atom, a process that does not racemize the skeletal chirality of **3**. If interchange of these two isomers is slow at -93°, two different resonances of unequal intensity should be observed for the ^tBu methyl resonances in the ^1H NMR. Indeed, at -93 °C the 400-MHz ^1H NMR show two signals at 1.58 and 1.51 ppm (relative intensity = 1:2.6) are observed which coalesce and average to a single peak at about -40 °C. At room temperature a single sharp peak is observed at 1.54 ppm which is the exact weighted average of the peaks observed at -93 °C after correction for changes in isomer population. These results present strong evidence for the existence of the cisoid and transoid isomers of **3** and their rapid interconversion above -40 °C.

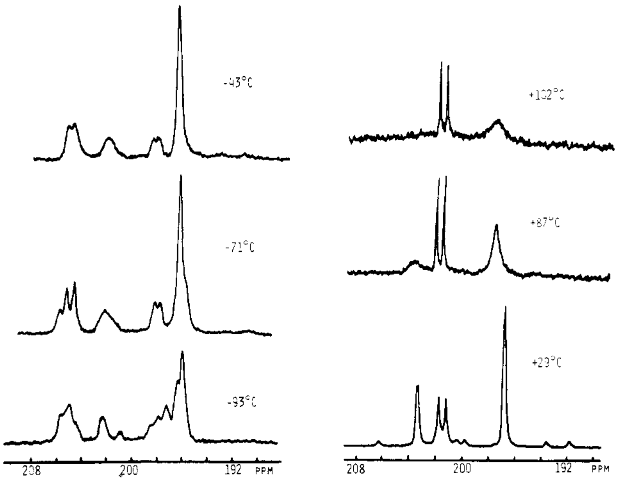
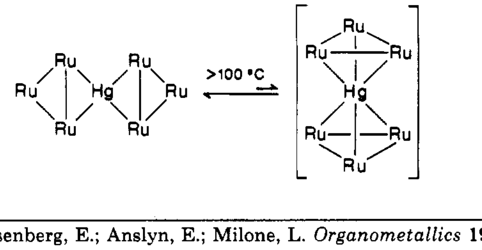


Figure 3. Variable-temperature ^{13}C NMR of **4b** in the carbonyl region from -93 to +102 °C (CD_2Cl_2, -93 to -42 °C; $C_6D_5CD_3$, -40 to +102 °C).

It has been shown through deuterium isotope effects[18] that in order for axial–radial exchange to take place on hydride-bridged metal centers the hydride bond must break or bend back onto one face of the metal cluster. It is suggested here that the same is true for systems containing the bridging mercury moiety. The bridging mercury atom must bend back under the cluster assuming a face-bridging mode. This rearrangement of the mercury then allows for axial–radial exchange to take place on the mercury-bridged rutheniums. Rapid axial–radial exchange is known to be a prerequisite to intermetallic scrambling. The suggestion here is that the intermediate structure necessary to allow intermetallic scrambling at high temperature contains a hexacoordinated mercury atom in a doubly face-bridging sandwich-type structure with the Ru triangles staggered with respect to each other. There is precedent for mercury adopting a μ_3 face-bridging mode in the ground state (eq 14).[6]



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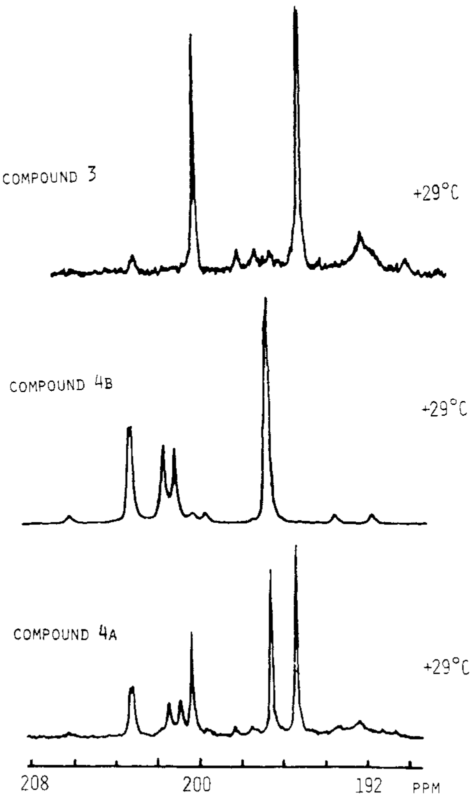


Figure 4. Comparison of room-temperature ^{13}C NMR spectra of 3, 4a, and 4b in the carbonyl region.

When two phosphines are substituted for two carbonyls on the wing-tip Ru atoms to form the bis derivative **4b**, no changes in the localized scrambling processes are observed. However, there is a pronounced effect on the observed intermetallic scrambling process at high temperature (Figure 3).

As the temperature is raised to 102 °C, the resonances assigned to the axial and radial carbonyls on the mercury-bridged edge of the cluster broaden and are coalesced into a single broad resonance at $\delta = 198.0$ ppm. The axial and radial carbonyls on the wing-tip ruthenium atoms remain as a sharp doublet at $\delta = 202.2$ ppm ($^2J(P-C) = 10.0$ Hz) indicating that they are not participating in any intermetallic scrambling at this temperature. The bulky phosphine ligand in its rapid pinwheel motion seems to prevent the mercury atom from shifting from the edge-bridging mode to the face-bridging mode. Without this required shift, the mercury-bridged edge of the triruthenium fragment remains sterically hindered, thus raising the barrier to intermetallic scrambling.

The interpretation of the variable-temperature ^{13}C NMR spectra of the mono(phosphine) derivative **4a** depends heavily on conclusions drawn from the ^{13}C NMR data of the more symmetrical clusters **3** and **4b**. The variable-temperature ^{13}C NMR of **4a** gives spectra which are the sum of the spectra of **3** and **4b** at the same temperature. For example, if the room-temperature spectrum of the unsubstituted cluster **3** is added to the spectrum of the bis-substituted cluster **4b**, the resulting composite spectrum is identical with that of **4a** (Figure 4). With these comparisons in mind we conclude that the dynamic behavior of the phosphine-substituted Ru_3 fragment in **4a** is the same as **4b** with the exception of the low-temperature-limiting spectrum where the greater number of conformers available to **4b** gives more CO resonances. Similarly the unsubstituted Ru_3 fragment in **4a** has the same dynamic properties as **3**. The two Ru_3 fragments thus behave independently with respect to their dynamic properties (Figure 4). This analysis is valid at all temperatures examined. The carbonyls on the phosphine-substituted, wing-tip ruthenium do not undergo intermetallic scrambling as observed for the bis(phosphine) derivative **4b**. This suggests a structure for an intermediate in which the unsubstituted triruthenium fragment allows the mercury to adopt a face-bridging mode, while the phosphine-substituted triruthenium fragment retains the mercury in the ground state, edge-bridging mode (eq 15).

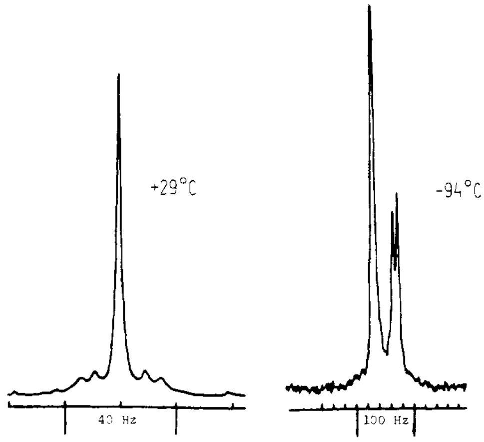
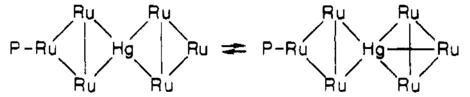


Figure 5. Variable-temperature ^{31}P NMR of **4a** in CD_2Cl_2 at 32 MHz.



(15)

Further evidence for this proposed rearrangement of the metal skeleton was obtained from an examination of the variable-temperature ^{31}P NMR of a mono(phosphine) derivative of **3** containing the chiral phosphine $P(CH_3)(C_6H_5CH_2)(C_6H_5)$ (see below).

L. Variable-Temperature ^{31}P NMR. The low-temperature proton-decoupled ^{31}P NMR spectrum of **4a** was observed at −94 °C and showed three resonances at 65.4, 64.4, and 64.1 ppm with relative intensities of 1:0.26:0.38 referenced to external H_3PO_4 (Figure 5). These three resonances are assigned to the three inequivalent positions (two radial and one axial) that the phosphine can occupy. The resonances of relative intensities 1.0 and 0.38 can be assigned to the two radial positions with one being more favored than the other for steric reasons. The conformer with the phosphine in the axial position, being the most sterically hindered, has the lowest population. This is in sharp contrast with the mono(phosphine) derivative $HRu_3(CO)_8(\mu_3\text{-}\eta^2\text{-}C_2{}^tBu)(PPh_3)$ (**1a**) which shows one resonance at similar temperatures indicating that only one radial position is occupied by the phosphine ligand in **1a** at 64.3 ppm at −94 °C. The reason for this difference seems to be steric in nature with one of the radial positions of **4a** being more crowded for the bulky phosphine as a result of the longe range interactions with carbonyl groups on the neighboring ruthenium atoms (Figure 1). Examination of the solid state structure of **3** does indeed reveal that the two radial positions on the wing-tip ruthenium have very different environments as a result of their difference in distance to the wing-tip ruthenium atom on the opposite wing. At room temperature (29 °C), the three phosphine peaks coalesce into one peak (64.9 ppm) as a result of averaging of the axial and two radial positions on the wing-tip ruthenium. It is possible that the "cis" and "trans" isomers proposed for **3** could also be present in

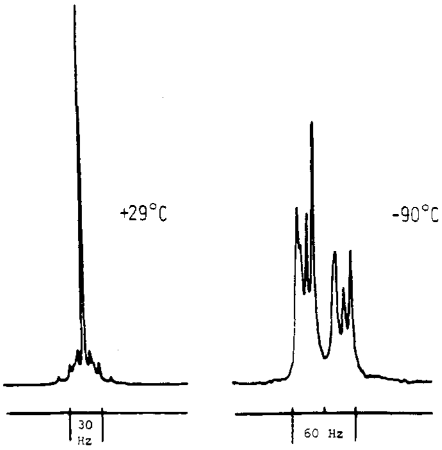


Figure 6. Variable-temperature ^{31}P NMR of **4b** in CD_2Cl_2 at 32 MHz.

solutions of **4a**, but it is not possible to ascertain their presence from these data.

The variable-temperature ^{31}P NMR of the bis(phosphine) derivative **4b** shows the same averaging process as discussed above (Figure 6). The low-temperature-limiting spectrum of **4b** at −90 °C shows at least eight partially overlapping resonances from 63.6 to 65.2 ppm. These resonances are assigned to the nine possible conformers expected when the two phosphines occupy the three possible positions accessible to each on the wing-tip rutheniums. The room-temperature (29 °C) spectrum of **4b** shows a single peak at 64.5 ppm arising from axial–radial averaging of the nine expected conformers.

When **3** is reacted with a racemic mixture of the chiral phosphine $P(CH_3)(C_6H_5CH_2)(C_6H_5)$, a mixture of the two sets of diastereomers (**4f**, **4f′**) is obtained which are not separable by standard thin-layer chromatographic techniques. At room temperature the proton-decoupled ^{31}P NMR (200 MHz) shows two resonances at 61.30 and 61.34 ppm separated by 7.5 Hz, corresponding to the two sets of diastereomers (Figure 7). At 55 °C, the two peaks appear sharpened as the rate of axial–radial exchange is increased. There is no indication of any process that averages the two sets of diastereomers at this temperature. However, at 100 °C, the spectrum shows that the two resonances have coalesced into one peak, indicating the onset of a process that averages the two sets of diastereomers.

Several mechanisms could account for the observed averaging of the two sets of diastereomers. First, a rearrangement of the metal framework to a structure which contains a plane of symmetry would racemize the mixture. The shift of the mercury from an edge-bridging mode to a face-bridging mode on one Ru_3 fragment proposed earlier to account for the observed carbonyl averaging process in **3** would also provide the necessary plane of symmetry to racemize the mixture.

Although the face-bridged intermediate proposed here is not a unique way to racemize the skeletal chirality of **3**, we feel it is more likely than the mercury adopting a square-planar configuration where transannular carbonyl interactions would be prohibitive. In addition, since we have shown that intermetallic carbonyl scrambling occurs at the same temperature as racemization, the intermediate that allows this to happen must have all three edges of each Ru_3 triangle available for carbonyl bridge formation. We feel that the face-bridged intermediate suggested here best explains the simultaneity of both processes. Furthermore, we can rule out racemization by a dissociative process since no redistribution to give a bis-substituted analogue of **4f** or **4f′** and **3** on the time scale of the NMR experiment was observed. The racemization of **4f** and **4f′** occurs with a rate constant of about 10^3 s^{-1} as estimated from a coalescence temperature of 100 °C. The redistribution reaction occurs with a pseudo-first-order rate constant of 10^{-2}–10^{-3} s^{-1} as estimated from an equilibration time of 4 h at 100 °C. Finally, it should be pointed out that the edge to face interconversion proposed here has been recently observed by Shriver et al. in the related cluster $Fe_4(CO)_{13}(\mu_3\text{-}Hg)\text{-}Mo(CO)_3(\eta\text{-}C_5H_5)$.[19]

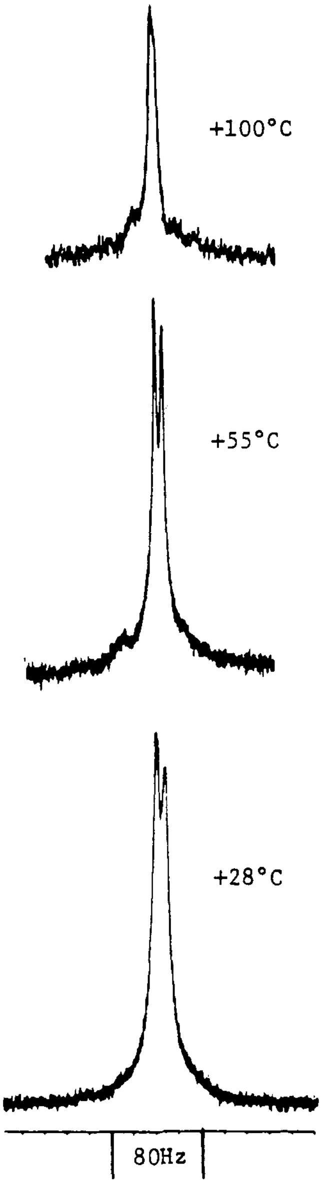


Figure 7. Variable-temperature ^{31}P NMR of **4f** and **4f′** in $CD_3C_6D_5$ at 200 MHz.

Experimental Section

Materials. Literature procedures were used for the preparation of $Ru_3(CO)_{12}$[20] and compounds **1**,[21] **1a**,[22] **2a**,[2] and **2b**.[2] $RuCl_3\cdot 3H_2O$ (Johnson-Matthey) was used as the source of ruthenium. Tetrahydrofuran (Mallinckrodt) was distilled from sodium benzophenone ketyl under a nitrogen atmosphere. All other solvents

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[19] Wang, J.; Sabat, M.; Horwitz, C. P.; Shriver, D. F. *Inorg. Chem.* **1988**, *27*, 552.

[20] Basolo, F. *Inorg. Synth.* **1976**, *XVI*, 47.

[21] Sappa, E.; Gambino, O.; Milone, L.; Cetini, G. *J. Organomet. Chem.* **1972**, *39*, 169.

[22] Rosenberg, E.; Skinner, D.; Milone, L.; Aime, S.; Sappa, E. *Inorg. Chem.* **1980**, *19*, 1571.

were reagent grade and dried over molecular sieves (4A) before use. Triphenylphosphine (Aldrich) and ethyl 3-diphenylphosphinopropionate (Strem) were used as supplied by the manufacturer without further purification. Benzylmethylphenylphosphine was prepared by reduction of the corresponding oxide with phenylsilane.[23] Deuteriated NMR solvents toluene-d_8, $CDCl_3$, and CD_2Cl_2 were dried over molecular sieves (4A).

Spectra. ^1H NMR spectra were measured on an IBM NR-80 spectrometer at 80 MHz and a Bruker AM-400 spectrometer at 400 MHz. ^{13}C NMR spectra were measured on an IBM NR-80 at 20 MHz and a Bruker WH-500 at 125 MHz by using samples 10–15% CO enriched. ^{13}C NMR solutions were 0.05 M in Cr(acac)$_3$ (Mallinckrodt). ^{31}P NMR spectra were measured on an IBM NR-80 at 32 MHz and a Bruker WH-500 at 200 MHz and referenced to external H_3PO_4. IR spectra were measured on a Sargeant-Welch/Pye Unicam SP3-100 spectrophotometer. All samples for ^{13}C NMR were scrupulously purified by preparative TLC before use.

Analysis. All elemental analyses were performed by Schwartzkopf Microanalytical Laboratories, New York, NY.

Preparation of 3. Although the synthesis of 3 has previously been reported,[3] an improved procedure will be presented here. A 250-mL, three-neck flask is equipped with a 25-mL pressure-equalizing dropping funnel, a magnetic stir bar, a glass inlet tube, and a gas adaptor attached to a mineral oil bubbler. The reaction vessel is flame-dried under nitrogen and then charged with $HRu_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_2{}^tBu)$ (1.243 g, 1.950 mmol). All further operations are done under a carbon monoxide atmosphere. Tetrahydrofuran (40 mL, freshly distilled from sodium benzophenone) is added by syringe and degassed thoroughly with carbon monoxide. To this solution is added degassed alcoholic potassium hydroxide (17.5 mL of 0.128 M, 2.24 mmol) dropwise through the addition funnel with continuous stirring. The resulting amber solution is allowed to stir for 1/2 h to ensure complete conversion to the $Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_2{}^tBu)$ anion. Mercuric iodide (0.444 g, 0.978 mmol) is dissolved in dry tetrahydrofuran (10 mL) degassed with carbon monoxide, and added to the reaction mixture by syringe. The resulting solution is allowed to stir under a carbon monoxide atmosphere until a bright yellow precipitate forms. The reaction time is typically 20–30 min. Upon precipitation, the reaction mixture is chilled and evaporated to half its original volume under reduced pressure. The resulting solution is filtered. The filtrate is then evaporated to dryness under reduced pressure, and the resulting residue is washed first with 25 mL of absolute ethanol followed by 25 mL of methylene chloride. The resulting yellow residue is combined with the initial precipitate and recrystallized from hot THF to yield 1.1580 g of 3 (80.6% yield based on 1). Anal. Calcd for $C_{30}H_{18}O_{18}HgRu_6$: C, 24.40; H, 1.22. Found: C, 24.63, H, 1.53.

Thermal Reaction of 3 and Trialkyl- (or Triaryl-) Phosphines. A. Triphenylphosphine. Due to the relative insolubility of *3* in hydrocarbon solvents large amounts of solvent were necessary. A 1.0-L flask is flamed out under dry nitrogen and charged with 3 (819.6 mg, 0.5564 mmol). Heptane (450 mL, dried over molecular sieves) is added to the flask and deaerated with nitrogen gas. To the resulting mixture is added triphenylphosphine (449.2 mg, 1.713 mmol, 3.1 molar excess), and the mixture is heated with stirring to reflux. After 4 h, the reaction mixture is cooled to room temperature and the solvent removed under reduced pressure (rotary evaporated). The resulting brownish orange residue is dissolved in the minimum amount of dry CH_2Cl_2 and chromatographed on 15 TLC plates (PF-254 silica gel) using 30% CH_2Cl_2/hexane mixture as eluent. Four bands were eluted: The top yellow band is 3 (38.4 mg). The second orange band is removed and recrystallized from hot hexane to yield **4a** (240.0 mg, 26.5% yield based on 3). The third and fourth orange-colored bands are also recrystallized from hot hexanes to yield **4b** (180.1 mg, 17.5%) and **4c** (25 mg, ~5%).

Compound 4a: IR (ν(CO), cm^{-1}; CH_2Cl_2) 2090 (s), 2040 (m), 1995 (m), 1975 (br); ^1H NMR (CD_2Cl_2, ppm) 1.41 (18, s), 7.45 (15, m); ^{31}P NMR (CD_2Cl_2) 64.89 ppm. Anal. Calcd for $C_{47}H_{33}O_{17}HgPRu_6$: C, 33.06; H, 1.95; P, 1.76. Found: C, 33.01; H, 2.05; P, 1.8.

Compound 4b: IR (ν(CO), cm^{-1}; CH_2Cl_2) 2050 (s), 2000 (m), 1996 (s), 1980 (s); ^1H NMR (CD_2Cl_2, ppm) 1.40 (9, s), 7.47 (15, m): ^{31}P NMR (CD_2Cl_2) 64.51 ppm. Anal. Calcd for $C_{64}H_{48}O_{16}HgP_2Ru_6$: C, 39.85; H, 2.65; P, 3.28. Found: C, 39.58, H, 2.49; P, 3.19.

Compound 4c: IR (ν(CO), cm^{-1}; CH_2Cl_2) 2040 (m), 2010 (m), 1985 (s, br), 1962 (s, br); ^1H NMR (CD_2Cl_2, ppm) 1.36 (18, s), 7.45 (45, m); ^{31}P NMR (CD_2Cl_2)/66.98 (s), 66.30 (s), 50.89 ppm (s) (^2J(HgP) = 573.6 Hz). Anal. Calcd for $C_{81}H_{63}O_{15}HgP_3Ru_6$: C, 44.74; H, 3.38. Found: C, 44.76, H, 2.99.

B. P(PPh)$_2$(CH$_2$CH$_2$COOC$_2$H$_5$). The reaction of 3 and P(Ph)$_2$(CH$_2$CH$_2$COOC$_2$H$_5$) is performed as above. 3 (316.1 mg, 0.2146 mmol) is dissolved in toluene (210 mL) and deaerated with nitrogen gas. P(Ph)$_2$(CH$_2$CH$_2$COOC$_2$H$_5$) (0.007 mL, 0.220 mmol, 1.03 molar excess) is added by syringe, and the mixture is heated to 90 °C by using an oil bath. After 7.5 h, the reaction mixture is cooled and the solvent is chromatographed as presented above to yield 3 (83.6 mg), **4d** (145.4 mg, 53.2% based on 3 consumed), and **4e** (39.6% based on 3 consumed).

Compound 4d: IR (ν(CO), cm^{-1}; CH_2Cl_2) 2080 (s), 2040 (s), 1979 (s, br), 1725 (m, organic C=O); ^1H NMR (CD_2Cl_2, ppm) 7.15 (10, m), 3.84 (2, q), 2.74 (4, m), 1.33 (9, s), 1.18 (9, s), 0.86 (3, t). Anal. Calcd for $C_{46}H_{37}O_{19}HgPRu_6$: C, 32.22; H, 2.25. Found: C, 31.88, H, 2.16.

Compound 4e: IR (ν(CO), cm^{-1}; CH_2Cl_2) 2090 (w), 2040 (s), 2010 (s), 1970 (br), 1725 (m, organic C=O); ^1H NMR (CD_2Cl_2, ppm) 7.43 (10, m), 4.05 (2, q), 2.68 (4, m), 1.31 (9, s), 1.21 (3, t). Anal. Calcd for $C_{62}H_{56}O_{20}HgP_2Ru_6$: C, 37.73; H, 2.91; P, 3.13. Found: C, 37.50, H, 2.84, P, 3.11.

C. P(CH$_3$)(CH$_2$C$_6$H$_5$)(C$_6$H$_5$). Compound 3 (403.7 mg, 0.2740 mmol) is dissolved in toluene (125 mL, dried over molecular sieves), and the resulting solution is degassed with nitrogen. To this solution is added $P(CH_3)(C_6H_5)(CH_2C_6H_5)$ (0.20 mL, 0.841 mmol) by syringe, and the mixture is refluxed for 2 h. The reaction mixture is purified by chromatography (10 TLC plates, 30% CH_2Cl_2/hexane mixture as an eluent). Two major bands were eluted. The top band was identified as 3 (139.2 mg). The second band was identified as **4f** (133.1 mg, 45% based on 3 consumed).

Compound 4f/4f′: IR (ν(CO), cm^{-1}; CH_2Cl_2) 2060 (sh), 2030 (s), 2010 (s), 1970 (br); ^1H NMR (CD_2Cl_2) 7.31 (10 m), 3.52 (2, m), 1.93 (3, d), 1.37 (18, s); ^{31}P NMR ($C_6D_5CD_3$) 61.30, 61.34 ppm. Anal. Calcd for $C_{43}H_{33}O_{17}PH_gRu_6$: C, 30.97; H, 2.28. Found: C, 31.12, H, 2.08.

Thermal Reaction of 3 and H$_2$. A 100-mL flask is flame-dried under N_2 and charged with 3 (102.2 mg, 0.06938 mmol) and 75 mL of dry octane (or heptane). The hydrogen gas and heat are turned on, and the reaction mixture is refluxed for $3^1/_2$ h (6 h if heptane is used). During the heating, the solution goes from yellow to dark green and a metal precipitate can be seen after 2 h. The solution is cooled and the solvent removed under reduced pressure. The resulting residue is chromatographed by using two TLC plates (PF-254 silica gel, hexane eluent). Four bands are eluted and recrystallized from a CH_2Cl_2/hexanes mixture. The top salmon-colored band was identified as 5 (23.4 mg, 26.3% yield based on 3). The second, yellow-colored band was identified as 1 (9.8 mg, 11.1% yield based on 3). The third, salmon-colored band was identified as $H_4Ru_4(CO)_{12}$ (11.6 mg, 15.0% yield based on 3). The fourth, yellow-colored band was identified as unreacted 3 (5.0 mg).

$H_4Ru_4(CO)_{12}$: IR (ν(CO), cm^{-1}; CH_2Cl_2) 2077 (s), 2062 (s), 2026 (w), 2021 (s) cm^{-1}; ^1H NMR ($CDCl_3$) -17.8 ppm. **5**: IR 2070 (s), 2030 (s), 2010 (s), 1995 (shoulder) cm^{-1}; ^1H NMR ($CDCl_3$, ppm, relative intensity) 4.39 (s, 2), 1.14 (s, 9), -17.5 (s, 3). **1**: IR 2097 (m), 2070 (s), 2054 (s), 2022 (s), 1992 (m) cm^{-1}, ^1H NMR 1.4 (s, 9), -21.8 (s, 1).

Photolysis of 3. A 65-mL, Pyrex (or quartz), water-jacketed, photochemical reaction vessel is charged with 3 (54.9 mg, 0.03727 mmol) and 50 mL of THF. The resulting solution is then degassed with nitrogen. The cooling water and the UV light (mercury vapor lamp) are turned on for 4 h. The solvent is then evaporated to dryness, and the residue is dissolved in the minimum amount of THF and chromatographed on one TLC plate (PF-254G silica gel, pure hexane used as eluent). Only the starting material 3 (50.1 mg, 91.2% recovery) and base-line decomposition products were present. Compound 3 was identified by ^1H NMR and IR spectra.

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[23] Rosenberg, E.; Milone, L.; Thorson, C. B.; Aime, S. *Inorg. Chem.* 1985, *24*, 231.

Photolysis of 3 and PPh_3. A 65-mL, Pyrex, water-jacketed, photochemical reaction vessel is fitted with a nitrogen gas line, and the vessel is flushed with dry nitrogen and after being charged with **3** (53.4 mg, 0.03625 mmol) and tetrahydrofuran (50 mL, freshly distilled from sodium benzophenone ketyl). Triphenylphosphine (15.2 mg, 0.580 mmol, 1.6 molar excess) is added to the solution which is irradiated with a medium-pressure mercury vapor lamp (125 W). The reaction is followed by analytical TLC. After 2 h, the analytical TLC plates show the presence of **4a** and **4b**, the lamp is shut off, and the solvent is removed under reduced pressure (rotary evaporated). The residue is chromatographed on one TLC preparative plate to yield: **3** (18.2 mg), **4a** (10.2 mg, 25.5% based on **3** consumed), and **4b** (5.2 mg, 11.4% based on **2** consumed). The phosphine-substituted products were identified by comparative TLC, NMR, and IR spectra.

Photolysis of 3 and H_2. A 65-mL, water-jacketed, Pyrex photochemical reaction vessel is fitted with a gas inlet tube is charged with **3** (51.5 mg, 0.03496 mmol) and dry THF (50 mL). The hydrogen gas and the UV source (mercury vapor lamp) are turned on for 35 min. The solvent is then evaporated under reduced pressure and the residue chromatograrphed on one TLC plate (PF-254G, 10% CH_2Cl_2/hexane eluent). Four bands are eluted: **5** (top band) (8.0 mg, 18.0% yield based on **3**). The second band is **1** (11.8 mg, 26.4% based on **3**). The third band is unreacted **3** (6.0 mg). The fourth, yellow band was not identified due to low yield (less than 5 mg recovered from the TLC plate).

Reaction of 3 with Sodium Benzophenone Ketyl. A 100-mL, two-neck flask equipped with a magnetic stir bar is flame-dried under N_2 and charged with **3** (102.1 mg, 0.06931 mmol), PPh_3 (26.3 mg, 0.1003 mmol, 1.45 molar excess), and 30 mL of THF (freshly distilled from sodium benzophenone under N_2). The resulting solution is deaerated with N_2 gas. To this solution was syringed sodium benzophenone ketyl (0.0693 mmol, 1.26 mL of a 0.055 M sodium benzophenone ketyl in THF) into the reaction vessel with stirring. The reaction mixture was stirred for 6 days at which point no further change in the reaction mixture was noted by analytical TLC, 20 mL of 0.1 M HCl was added, and the entire mixture was dried and then extracted into CH_2Cl_2. The CH_2Cl_2 fractions were combined and evaporated to dryness under reduced pressure. The resulting residue was redissolved in the minimum amount of CH_2Cl_2 and chromatographed on three TLC plates (PF-254G silica gel with a 20% CH_2Cl_2/hexane solution as an eluent). Three bands were eluted. The top band was identified as **1** (11.0 mg, 20.5% conversion of **3**). The second band was identified as unreacted starting material, **3** (40 mg). The third band was identified as **4a** (10.3 mg, 14.3% conversion of **3**). When 2 equiv of sodium benzophenone ketyl are used, only **1** is obtained. Products were identified by their IR and NMR spectra.

Reaction of 3 with Br_2. A 100-mL, two-neck flask is equipped with a nitrogen gas line and a magnetic stir bar. The flask is flame-dried under nitrogen and charged with **3** (47.7 mg, 0.03238 mmol) and 30 mL of dry THF. Br_2 (5.1 μL, 0.09714 mmol) dissolved in 3 mL of THF is added to the reaction mixture by syringe. The resulting mixture is stirred for four days at room temperature, then the solvent is removed by evaporation under reduced pressure. The residue remaining is chromatographed on one TLC plate (50% CH_2Cl_2/hexane used as eluent). Two bands were eluted and recovered from the plate. A yellow base-line product was not taken. The two bands were identified as **2b** (6.5 mg, 22.4% yield based on **3**) and unreacted starting material, **3** (13.0 mg). The product was identified by ^1H NMR and IR spectra. Compound **2b**: IR (ν(CO), cm^{-1}; CH_2Cl_2) 2090 (w), 2050 (s), 2000 (s), 1995 (w); ^1H NMR 1.36 ppm (s).

Reaction of 3 with HCl. A 250-mL, three-neck flask is equipped with a nitrogen line, a stir bar, and a gas inlet tube to be used to bubble HCl through the solution. The flask is flame-dried, and 175 mL of dry toluene is added. Dry HCl is bubbled through the toluene for $^1/_2$ h. The HCl is then shut off, the nitrogen turned on, and **3** (53.9 mg, 0.03659 mmol) is added. The resulting solution is allowed to stir for 18 h. Nitrogen gas is then vigorously bubbled through the solution to purge the system of HCl. When the solution is neutral to pH paper, the solvent is removed under reduced pressure. The residue is chromatographed on one TLC plate (40% CH_2Cl_2/hexane solution used as an eluent). Three bands were eluted. The top band was identified as **1** (7.7 mg, 33.0% yield based on **3**). The second band was starting material, **3** (7.0 mg). The third band was identified as $(\mu_3\text{-}\eta^2\text{-}C_2{}^tBu)(CO)_9Ru_3(\mu\text{-}Hg)Cl$ (**2c**) (5.8 mg, 18.2% yield based on **3**). Compound **2c**: ^1H NMR 1.36 ppm (s).

Reaction of 3 and Ethanethiol. A 250-mL, three-neck flask is equipped with a carbon monoxide gas line, a water-cooled reflux condenser, and a magnetic stir bar. The reaction vessel is flame-dried under nitrogen and charged with **3** (204.1 mg, 0.1383 mmol) and dry THF (150 mL). Ethanethiol (0.050 mL, 0.67 mmol) is added by syringe, and the resulting reaction mixture is refluxed under a CO atmosphere. After 1 day, an orange precipitate forms. Analytical TLC plates at this tme show the formation of **1**. The solution is allowed to reflux for 3 days after which the orange-brown precipitate (93.7 mg) is filtered and the filtrate evaporated to dryness. The residue obtained from the filtrate is chromatographed by preparative TLC (four TLC plates, 10% CH_2Cl_2/hexane mixture used as eluent). Two yellow bands are eluted and recrystallized from hexanes at −20 °C. The top yellow band was identified as **1** (43.3 mg, 60.1% conversion based on **3** consumed). The second yellow band was identified as unreacted **3** (37.5 mg). The brown-orange precipitate, which smelled strongly of sulfur, was insoluble in all solvents tried (CH_2Cl_2, $CHCl_3$, THF, hexane) and was not further identified.

Reaction of 3 with Zn Metal. A 250-mL, three-neck flask is equipped with a water-cooled, reflux condenser, a magnetic stir bar, and a gas inlet tube. The flask is flame-dried and charged with **3** (108.1 mg, 0.07338 mmol), dry heptane (100 mL), and Zn metal (136.1 mg, 20 mesh, freshly washed with dilute HCl, distilled water, and acetone, then thoroughly dried under a stream of N_2 before use). Carbon monoxide is bubbled through the reaction mixture while the solution is refluxed for 14 h. The solvent is then evaporated under reduced pressure, and the resulting residue was chromatographed on three preparative TLC plates (20% CH_2Cl_2/hexane mixture used as eluent). Two bands were removed and identified as **1** (8.0 mg, 8.6% yield based on **1**) and $Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_2{}^tBu)]_2Zn$ (89.0 mg, 90.7% yield based on **3**).

IR (ν(CO), cm^{-1}; CH_2Cl_2): 2080 (w), 2060 (s), 2005 (m), 1995 (m). ^1H NMR ($CDCl_3$): 1.5 ppm. Anal. Calcd for $C_{30}H_{18}O_{18}Ru_6Zn$: C, 26.93; H, 1.36; Zn, 4.86. Found: C, 26.74; H, 1.53; Zn, 5.02.

Thermolysis of 4d under CO Atmosphere. A 50-mL, three-neck flask is fitted with a water-cooled, reflux condenser, a gas inlet tube used to bubble CO through the reaction mixture, and a magnetic stir bar. The reaction vessel is flame-dried under nitrogen and charged with **4d** (25.3 mg, 0.01461 mmol) and benzene (20 mL dried over sodium). The CO gas and heat are turned on, and the solution is refluxed for 10 h. After heating, the reaction mixture is cooled at room temperature and the solvent is removed under reduced pressure. The resulting residue is chromatographed on one preparative TLC plate (25% CH_2Cl_2/hexane eluent). Three bands were eluted and identified as **3** (3.6 mg), **4d** (13.7 mg), and **4e** (5.0 mg). A smaller scale reaction was followed by ^1H NMR in toluene-d_8. Integration of the *tert*-butyl methyl resonances gave approximately the same value for the redistribution equilibrium constant as that obtained for the longer scale reaction (i.e., ~0.1).

Acknowledgment. We gratefully acknowledge the National Science Foundation (CHE 8711549) for support of this research. We also acknowledge the Regional NMR Facility at the California Institute of Technology for help in obtaining high-field NMR spectra and R. Perrigan and Dr. A. Fratiello at California State University, Los Angeles, for obtaining 400-MHz ^1H NMR.

Registry No. 1, 57673-31-1; **2b**, 74870-34-1; **2c**, 117917-34-7; 3, 84802-26-6; **4a**, 117917-28-9; **1b**, 117917-29-0; **1c**, 117917-30-3; **4d**, 117917-31-4; **4e**, 117917-32-5; **4f**, 117917-33-6; **4f′**, 118013-32-4; 5, 79075-59-5; $H_4Ru_4(CO)_{12}$, 34438-91-0; Zn, 7440-66-6; $[Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_2{}^tBu)]_2Zn$, 117917-35-8; sodium benzophenone ketyl, 3463-17-0; mercuric iodide, 7774-29-0; ethanethiol, 75-08-1.